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(54) ALKALINE STORAGE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To increase the utilization factor at a high temperature while maintaining the battery performance of a nickel positive electrode by applying a single substance or a compound of rare earth elements on the surface of the nickel electrode mainly made of nickel hydroxide.

SOLUTION: A single substance or a compound of rare earth elements is slightly dissolved in an alkaline aqueous solution and deposited as a stable hydroxide. This hydroxide has an effect to raise the oxygen overvoltage at a high temperature, the generation of oxygen gas from the positive electrode side at the terminal stage of an electric charge is suppressed, and the utilization factor at a high temperature can be increased. When a single substance or a compound of rare earth elements is added, a film is formed when the rare earth element ions slightly eluted in an electrolyte are deposited on the surface of a hydrogen storage alloy electrode as a stable hydroxide, and the battery life is extended because the film prevents the corrosion of the alloy. This action is prominent in particular for ytterbium which is one of the rare earth elements.

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CLAIMS

[Claim(s)]

[Claim 1] The alkaline battery characterized by applying the simple substance or compound of rare earth elements to the front face of the nickel electrode which uses said nickel hydroxide as a principal component in the alkaline battery equipped with the separator and the alkali electrolytic solution which intervene between the positive electrode which consists of a nickel electrode which uses nickel hydroxide as a principal component, a negative electrode, and a positive electrode and a negative electrode.

[Claim 2] The alkaline battery according to claim 1 said whose rare earth elements are ytterbiums.

[Claim 3] The alkaline battery according to claim 1 whose compound of said rare earth elements is the hydroxide or oxide of an ytterbium.

[Claim 4] The alkaline battery characterized by applying the simple substance or compound of rare earth elements to the front face of said separator in the alkaline battery equipped with the separator and the alkali electrolytic solution which intervene between the positive electrode which consists of a nickel electrode which uses nickel hydroxide as a principal component, a negative electrode, and a positive electrode and a negative electrode.

[Claim 5] The alkaline battery according to claim 4 said whose rare earth elements are ytterbiums.

[Claim 6] The alkaline battery according to claim 4 whose compound of said rare earth elements is the hydroxide or oxide of an ytterbium.

[Claim 7] The alkaline battery according to claim 4 with which the simple substance or compound of said rare earth elements is applied to the field of the side which touches a positive electrode at least of said separator.

[Claim 8] The alkaline battery according to claim 1 or 4 the simple substance of said rare earth elements or whose coverage of a compound is 0.1 % of the weight - 10 % of the weight to the amount of positive active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the alkaline battery which used the nickel hydroxide as positive active material.

[0002]

[Description of the Prior Art] The positive electrode using a nickel hydroxide as an active material is broadly used in common with alkaline batteries, such as a nickel-hydride cell, a nickel-cadmium battery, a nickel-zinc cell, and a nickel-iron cell. Especially in recent years, a nickel-hydride cell attracts attention from viewpoints, such as low-pollution nature and a high energy consistency, and researches and developments are broadly made from the object for portable devices to the object for electric vehicles.

[0003] Since these alkaline cells are dedicated in the limited narrow space, such as a portable device and an electric vehicle, in any case, it was easy to carry out the temperature rise of them, and they have been set under the situation of being hard to radiate heat. For this reason, although the utilization factor maintenance at the time of the elevated temperature of positive active material is required, the cadmium addition to the positive active material which is one of the approaches for solving this has an environment top problem, and it will move against having low-pollution-ized from the nickel-cadmium battery to the nickel-hydride cell. Moreover, although the approach of adding a lithium-hydroxide water solution in the potassium-hydroxide water solution which is the electrolytic solution, and the approach of adding cobalt in the state of dissolution during the crystal of nickel hydroxide are proposed, when these means are adopted, the further cure is needed to the improvement in the engine performance of those other than the charging efficiency under an elevated temperature, and it cannot be said to be sufficient solution. Furthermore, in order to solve the problem of the utilization factor maintenance at the time of an elevated temperature, addition of a rare earth compound etc. is reported. However, in addition of a rare earth compound, the dissolution depressor effect of the surrounding matter was large, in order to also control the dissolution of the cobalt compound added as an electric conduction adjuvant in a positive electrode, forming [of the conductive network between active materials] became inadequate, and there was a problem that the high-rate-discharge engine performance fell.

[0004]

[Problem(s) to be Solved by the Invention] It tends to offer the alkaline battery which raised the utilization factor at the time of an elevated temperature, this invention being made in view of the above-mentioned trouble, and maintaining cell engine performance, such as high-rate-discharge engine performance of a nickel positive electrode.

[0005]

[Means for Solving the Problem] The 1st is an alkaline battery characterized by applying the simple substance or compound of rare earth elements to the front face of the nickel electrode which uses

said nickel hydroxide as a principal component in the alkaline battery equipped with the separator and the alkali electrolytic solution which intervene between the positive electrode which consists of a nickel electrode which uses the nickel hydroxide of this invention as a principal component, a negative electrode, and a positive electrode and a negative electrode. The 2nd of this invention is an alkaline battery said whose rare earth elements are ytterbiums. The 3rd of this invention is an alkaline battery whose compound of said rare earth elements is the hydroxide or oxide of an ytterbium. The 4th is an alkaline battery characterized by applying the simple substance or compound of rare earth elements to the front face of said separator in the alkaline battery equipped with the separator and the alkali electrolytic solution which intervene between the positive electrode which consists of a nickel electrode which uses the nickel hydroxide of this invention as a principal component, a negative electrode, and a positive electrode and a negative electrode. The 5th of this invention is an alkaline battery whose rare earth elements of said 4th invention are ytterbiums. The 6th of this invention is an alkaline battery whose compound of the rare earth elements of said 4th invention is the hydroxide or oxide of an ytterbium. The 7th of this invention is an alkaline battery with which the simple substance or compound of rare earth elements of said 4th invention is applied to the field of the side which touches a positive electrode at least of said separator. The 8th of this invention is an alkaline battery the simple substance of the rare earth elements of said the 1st or 4th invention or whose coverage of a compound is 0.1 % of the weight - 10 % of the weight to the amount of positive active material.

[0006] In an alkali water solution, an ytterbium or a ytterbium compound dissolves slightly and deposits as a stable hydroxide. Since an ytterbium hydroxide has the effectiveness of pulling up the oxygen overvoltage at the time of an elevated temperature and controls oxygen gas generating from the positive-electrode side in the charge last stage, it can raise the utilization factor in an elevated temperature. Moreover, if the simple substance or compounds of rare earth elements, such as an ytterbium, are added, a battery life will be extended, in order that a coat may be formed and this may prevent the corrosion of an alloy, in case the rare-earth-elements ion slightly eluted in the electrolytic solution deposits as a stable hydroxide in a hydrogen storing metal alloy electrode surface. Although these operations are looked at by general rare earth elements, the effectiveness of especially an ytterbium is large.

[0007] On the other hand, an ytterbium or the dissolution depressor effect of a ytterbium compound is $HCoO_2$ which also attains to a cobalt compound and a cobalt compound comes to dissolve. - It will carry out to control of generation of ion. If it becomes so, it will become inadequate forming [of the conductive network between the active materials by $CoOOH$ formed of charge of 1 cycle eye], and a utilization factor fall and high-rate-discharge degradation will be caused. However, since spreading on an ytterbium or the positive-electrode front face of a ytterbium compound can ensure conductive network formation by detaching the distance of an ytterbium or a ytterbium compound, and a cobalt compound, without controlling the dissolution of the cobalt compound inside a plate, the above evils are lost.

[0008] Moreover, the coverage of an ytterbium or a ytterbium compound has 0.1 % of the weight - 10 desirable % of the weight to the amount of positive active material. The oxygen-overvoltage rise effectiveness is not acquired as it is 0.1 or less % of the weight, but dissolution depressor effect is too large in it being 10 % of the weight or more, and the evil of activation of poor formation of a conductive network and the hydrogen storing metal alloy of a negative electrode being delayed appears.

[0009] Moreover, the oxygen overvoltage of nickel hydroxide can be similarly made high appropriately by applying the simple substance or compound of rare earth elements to a separator front face. In order not to have a bad influence on the conductive network formed of a dissolution deposit of a cobalt compound moreover, a utilization factor fall or high-rate-discharge degradation of a nickel electrode are not caused. Moreover, in order not to reduce the true nickel hydroxide fill in a nickel electrode, electrode capacitance or cell capacity falls and energy density does not fall.

[0010] Therefore, by producing an alkaline battery using these approaches, decline in the charging efficiency under an elevated temperature can be controlled without reducing the discharge potential and the electrode capacitance of a nickel electrode, and energy density, and the alkaline battery excellent in the charge-and-discharge effectiveness under wide range temperature can be offered.

[0011]

[Embodiment of the Invention] Hereafter, this invention is explained based on an example.

[0012] (Example 1) The high density nickel hydroxide which carried out solid-solution addition of Zn and the Co as positive active material was prepared, and 10 % of the weight (CoO) of 1 cobalt oxide was enough mixed as an electric conduction adjuvant, and the thickener was added to this, and it was made the shape of a paste, it pressed in the three-dimension porous body nickel substrate at thickness predetermined [after restoration and desiccation], and the positive-electrode plate was obtained. The paste which mixed the oxidization ytterbium (Yb 2O3) and the thickener to this was applied so that it might become 2.5 % of the weight to the amount of nickel hydroxide, and it dried again, and considered as this invention electrode. Moreover, the usual electrode which does not apply an oxidization ytterbium in the same procedure as the above was produced, and it considered as the reference electrode 1. Furthermore, 10 % of the weight of 1 cobalt oxide and 2.5 % of the weight of oxidization ytterbiums were enough mixed to the high density nickel hydroxide which carried out solid-solution addition of Zn and the Co, and the thickener was added to this, and it was made the shape of a paste, it pressed in the three-dimension porous body nickel substrate at thickness predetermined [after restoration and desiccation], and the positive-electrode plate was obtained. This was made into the reference electrode 2.

[0013] Thus, the charge and discharge test (charge 0.1C, discharge 0.2C) was performed under the overelectrolytic solution as the electrolytic solution, using a mercury oxide electrode as the potassium-hydroxide water solution of specific gravity 1.28, and a reference pole, having used the hydrogen storing metal alloy electrode as the counter electrode for this invention electrode, the reference electrode 1, and reference electrode 2 which were produced. A charge-and-discharge result is shown in drawing 1. this invention electrode had the high utilization factor compared with the reference electrode 1 which does not apply an oxidization ytterbium, and the difference appeared notably in the elevated temperature which are 50 degrees C and especially 40 degrees C. Moreover, the reference electrode 2 which mixed the oxidization ytterbium also showed the utilization factor equivalent to this invention electrode.

[0014] The charging curve (20 degrees C and 50 degrees C) of this invention electrode and a reference electrode 1 is shown in drawing 2. Although the oxygen overvoltage is comparable in 20 degrees C, in 50 degrees C, a reference electrode 1 does not have the standup of an oxygen overvoltage in the charge last stage, and that charge acceptance is falling hears. On the other hand, in this invention electrode, the standup of an oxygen overvoltage is seen in the charge last stage, and that charge acceptance is not falling in 50 degrees C hears. The same was said of the reference electrode 2 which mixed the oxidization ytterbium about the utilization factor maintenance at the time of an elevated temperature. This is based on the oxygen-overvoltage rise effectiveness of the oxidization ytterbium currently applied or mixed.

[0015] The charging curve of 1 cycle eye of this invention electrode, a reference electrode 1, and a reference electrode 2 is shown in drawing 3. The part of the reversible electrode potential looked at by 50-100mV shows the conductive network formation reaction expressed by (1) type.



[0016] It is expected that the reference electrode 2 which mixed the oxidization ytterbium has the short reaction expressed with (1) type since the part of reversible electrode potential is short, and conductive network formation is inadequate. This is based on the dissolution depressor effect of an oxidization ytterbium. Since the ytterbium was applied to the electrode surface in this invention electrode, since the dissolution of 1 cobalt oxide CoO took place smoothly, inside the electrode, conductive network formation was enough, and formation of the reference electrode 1 which does

not contain an oxidization ytterbium, and a conductive network was [inside] almost equivalent. [0017] The high-rate-discharge property of this invention electrode, a reference electrode 1, and a reference electrode 2 is shown in drawing 4. The reference electrode 2 which mixed the oxidization ytterbium has the large fall of a high-rate-discharge property compared with this invention electrode and a reference electrode 1. Since formation of a conductive network was inadequate as mentioned above and the high-rate-discharge property fell greatly, it thinks. Since this invention electrode had enough formation of a conductive network, the big fall of the high-rate-discharge engine performance was not seen.

[0018] (Example 2) The thing which applied to homogeneity what mixed the water solution which dissolved the oxidization ytterbium (Yb 2O3) and the thickener, and was made into the shape of a paste, and both sides of a commercial polyolefine system nonwoven fabric were made to dry first was produced. A three-dimension porous body nickel substrate is filled up with what mixed 10 % of the weight (CoO) of 1 cobalt oxide as an electric conduction adjuvant to the high density nickel hydroxide powder which made this the separator and carried out solid-solution addition of Zn and the Co. Use as a positive electrode the nickel electrode which pressed in thickness predetermined [after desiccation] and was produced, and a three-dimension porous body nickel substrate is filled up with a hydrogen storing metal alloy. By using as a negative electrode the hydrogen storing metal alloy electrode which pressed in thickness predetermined [after desiccation] and was produced, the electrode group of positive-electrode capacity regulation was constituted, the sealing form nickel-hydride battery was produced, using the potassium-hydroxide water solution of specific gravity 1.28 as the electrolytic solution, and it considered as this invention cell A.

[0019] (Example 3) What mixed the water solution which dissolved the oxidization ytterbium and the thickener in one side of the still more nearly same commercial polyolefine system nonwoven fabric as the above-mentioned example 2, and was made into the shape of a paste was applied to homogeneity, and what was dried was produced. The field which applied the oxidization ytterbium for this was used so that a nickel electrode might be touched, and it considered as the separator, and other conditions produced this invention cell B made the same as that of an example 2.

[0020] (Example of a comparison) The field which applied the oxidization ytterbium to one side again using what applied the oxidization ytterbium as well as the above-mentioned example 3 was used so that a hydrogen storing metal alloy electrode might be touched, and it considered as the separator, and other conditions produced the comparison cell C made the same as that of an example 2.

[0021] (Conventional example), making the polyolefine system nonwoven fabric of the same marketing as the above-mentioned example and the example of a comparison into the separator as it was on the other hand, other conditions produced Cell D conventionally which was made the same as that of an example 2.

[0022] thus, the thing to which the potential between two poles makes discharge 1 cycle by the current of 15-hour charge and 0.2C with the current of 0.1C of the geometric capacity of a nickel electrode until it results in 1V after leaving the produced various cells after pouring in in ordinary temperature for 48 hours -- 5 cycle repeat -- it was fully activated. The charge and discharge test was performed using these cells after that.

[0023] First, the result of having performed the temperature characteristic trial is shown in drawing 5 about Cell D the above-mentioned this invention cells A and B, the comparison cell C, and conventionally. In addition, under [various] temperature, a test condition discharges after charging with the current of 0.1C of the geometric capacity of a nickel electrode for 15 hours until the potential between two poles results in 1V with the current of 0.2C. It turns out that the capacity recovery when holding capacity sufficient also at the time of elevated-temperature charge and discharge by this invention cells A and B and the comparison cell C, and returning to ordinary temperature from drawing 5 is also good. Moreover, this effectiveness understands the field which applied the oxidization ytterbium also for a remarkable thing especially in this invention cells A and B used so that a nickel positive electrode might be touched. Since the oxygen overvoltage of nickel

hydroxide becomes high by having applied the oxidization ytterbium to the separator, this can enlarge the potential difference of a charge reaction and an oxygen gas generating reaction, and is considered to be because it to have become possible to raise charging efficiency.

[0024] Furthermore, Cell D was disassembled after test termination the above-mentioned this invention cells A and B, the comparison cell C, and conventionally, the active material after discharge was picked out from the nickel positive electrode and the hydrogen storing metal alloy negative electrode, respectively, and the X diffraction analyzed, after carrying out rinsing desiccation.

[0025] First, what expanded the X diffraction pattern of nickel positive active material and its part is shown in drawing 6. In addition, what expanded as reference a part of X diffraction pattern in the condition of having mixed the nickel positive-active-material raw material to drawing 6 is shown. clear from drawing 6 -- as -- this invention cells A and B, the comparison cell C, and the former -- Cell D -- any -- beta-nickel (OH) 2 A peak is main and most peaks of the 1 cobalt oxide (CoO) mixed as an electric conduction adjuvant are not seen. This is the result of showing that formation of a cobalt conductivity network is performed enough also in any of this invention cells A and B and the comparison cell C, without active jamming of a dissolution deposit of the 1 cobalt oxide by the dissolution depressor effect of an oxidization ytterbium influencing so greatly.

[0026] Next, what expanded the part among the X diffraction patterns of a hydrogen storing metal alloy negative-electrode active material is shown in drawing 7. In addition, a part of X diffraction pattern of the hydrogen storing metal alloy in front of charge and discharge is shown in drawing 7 as reference. Although the peak of the rare earth hydroxide by the corrosion of an alloy has appeared near theta= 27 degrees - 2 29 degree by Cell D conventionally so that clearly from drawing 7 , also in any of this invention cells A and B and the comparison cell C, this peak is small, and it turns out that the corrosion of an alloy is controlled.

[0027] As mentioned above, this invention cells A and B control decline in the charging efficiency under an elevated temperature, without reducing the discharge potential and the electrode capacitance of a nickel electrode, and energy density the comparison cell C and conventionally as compared with Cell D, the alloy corrosion of a hydrogen storing metal alloy negative electrode is controlled it not only excelled in the charge-and-discharge effectiveness under wide range temperature, but, and it turns out that it is the nickel-hydride battery excellent in the cycle life.

[0028] In addition, in this example, although the oxidization ytterbium (Yb 2O3) was used, when the hydroxylation ytterbium (Yb3 (OH)) was used, or also when an oxidization erbium (Er 2O3) and a hydroxylation erbium (Er3 (OH)) are used, equivalent effectiveness is acquired. Moreover, effectiveness is acquired about other rare earth elements. Although the nickel-hydride battery was produced in this example, equivalent effectiveness will be acquired if it is a nickel cadmium battery and the alkaline battery using the paste type nickel electrode which uses nickel hydroxide, such as a zinc nickel oxide battery, as a principal component as a positive electrode.

[0029]

[Effect of the Invention] As mentioned above, with the alkaline battery of this invention, the utilization factor of the nickel positive electrode under wide range temperature is raised, decline in the utilization factor under an elevated temperature is controlled, and since formation of the conductive network in an initial charge is also enough, the extremely excellent effectiveness that raise a high-rate-discharge property and stable capacitance characteristics and the outstanding cycle engine performance are obtained is acquired.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the relation between the number of cycles, and a utilization factor.

[Drawing 2] It is drawing having shown the charging curve in 20 degrees C and 50 degrees C.

[Drawing 3] It is drawing having shown the charging curve of 1 cycle eye.

[Drawing 4] It is drawing having shown the relation between a discharge rate and a utilization factor.

[Drawing 5] It is drawing showing the number of cycles when performing a temperature characteristic trial, and the relation of discharge capacity.

[Drawing 6] It is drawing expanding and showing the X diffraction pattern of the active material picked out from the nickel positive electrode, and its part.

[Drawing 7] It is drawing expanding and showing a part of X diffraction pattern of the active material picked out from the hydrogen storing metal alloy negative electrode.

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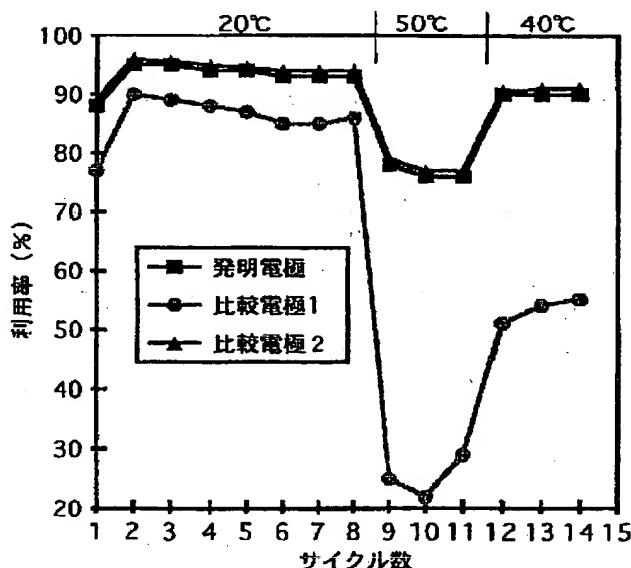
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(54)【発明の名称】 アルカリ蓄電池

(57)【要約】

【目的】ニッケル正極の高率放電性能などの電池性能を維持しつつ、高温時の利用率を高めたアルカリ蓄電池を提供することを目的とする。

【構成】水酸化ニッケルを主成分とするニッケル電極からなる正極と、負極と、正極と負極との間に介在するセパレータおよびアルカリ電解液とを備えたアルカリ蓄電池において、前記水酸化ニッケルを主成分とするニッケル電極の表面又は前記セパレータの表面に希土類元素の単体または化合物を塗布したアルカリ蓄電池とすることで、上記目的を達成できる。



【特許請求の範囲】

【請求項1】水酸化ニッケルを主成分とするニッケル電極からなる正極と、負極と、正極と負極との間に介在するセパレータおよびアルカリ電解液とを備えたアルカリ蓄電池において、前記水酸化ニッケルを主成分とするニッケル電極の表面に希土類元素の単体または化合物を塗布したことを特徴とするアルカリ蓄電池。

【請求項2】前記希土類元素が、イッテルビウムである請求項1記載のアルカリ蓄電池。

【請求項3】前記希土類元素の化合物が、イッテルビウムの水酸化物または酸化物である請求項1記載のアルカリ蓄電池。

【請求項4】水酸化ニッケルを主成分とするニッケル電極からなる正極と、負極と、正極と負極との間に介在するセパレータおよびアルカリ電解液とを備えたアルカリ蓄電池において、前記セパレータの表面に希土類元素の単体または化合物を塗布したことを特徴とするアルカリ蓄電池。

【請求項5】前記希土類元素が、イッテルビウムである請求項4記載のアルカリ蓄電池。

【請求項6】前記希土類元素の化合物が、イッテルビウムの水酸化物または酸化物である請求項4記載のアルカリ蓄電池。

【請求項7】前記希土類元素の単体または化合物が、前記セパレータの少なくとも正極に接する側の面に塗布されている請求項4記載のアルカリ蓄電池。

【請求項8】前記希土類元素の単体または化合物の塗布量が、正極活物質量に対して0.1重量%～10重量%である請求項1又は4記載のアルカリ蓄電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はニッケル水酸化物を正極活物質として用いたアルカリ蓄電池に関するものである。

【0002】

【従来の技術】ニッケル水酸化物を活物質として用いる正極は、ニッケル-水素化物電池、ニッケル-カドミウム電池、ニッケル-亜鉛電池、ニッケル-鉄電池などのアルカリ蓄電池に共通して幅広く用いられている。近年においては低公害性、高エネルギー密度などの観点から特にニッケル-水素化物電池が注目され、ポータブル機器用から電気自動車用まで幅広く研究開発がなされている。

【0003】これらアルカリ電池はいずれの場合でも、ポータブル機器や電気自動車等の限られた狭い空間の中に納められているため、温度上昇し易く、放熱しにくい状況下におかれている。このため、正極活物質の高温時の利用率維持が要求されるが、これを解決するための方法の一つである正極活物質へのカドミウム添加は環境上問題があり、ニッケル-カドミウム電池からニッケル-

水素化物電池へと低公害化してきたことに逆行することになってしまう。また、電解液である水酸化カリウム水溶液に、水酸化リチウム水溶液を添加する方法や、水酸化ニッケルの結晶中にコバルトを固溶状態で添加する方法が提案されているが、これらの手段を採用した場合、高温下での充電効率以外の性能向上に対して更なる対策が必要となり、充分な解決策とは言えない。更に高温時の利用率維持の問題を解決するためには希土類化合物などの添加が報告されている。しかし、希土類化合物の添加においては、周囲の物質の溶解抑制効果が大きく、正極中に導電補助剤として添加しているコバルト化合物の溶解も抑制してしまうため、活物質間ににおける導電性ネットワークの形成が不十分となり、高率放電性能が低下するという問題があった。

【0004】

【発明が解決しようとする課題】本発明は上記問題点に鑑みてなされたものであり、ニッケル正極の高率放電性能などの電池性能を維持しつつ、高温時の利用率を高めたアルカリ蓄電池を提供しようとするものである。

【0005】

【課題を解決するための手段】本発明の第1は、水酸化ニッケルを主成分とするニッケル電極からなる正極と、負極と、正極と負極との間に介在するセパレータおよびアルカリ電解液とを備えたアルカリ蓄電池において、前記水酸化ニッケルを主成分とするニッケル電極の表面に希土類元素の単体または化合物を塗布したことを特徴とするアルカリ蓄電池である。本発明の第2は、前記希土類元素が、イッテルビウムであるアルカリ蓄電池である。本発明の第3は、前記希土類元素の化合物が、イッテルビウムの水酸化物または酸化物であるアルカリ蓄電池である。本発明の第4は、水酸化ニッケルを主成分とするニッケル電極からなる正極と、負極と、正極と負極との間に介在するセパレータおよびアルカリ電解液とを備えたアルカリ蓄電池において、前記セパレータの表面に希土類元素の単体または化合物を塗布したことを特徴とするアルカリ蓄電池である。本発明の第5は、前記第4の発明の希土類元素が、イッテルビウムであるアルカリ蓄電池である。本発明の第6は前記第4の発明の希土類元素の化合物が、イッテルビウムの水酸化物または酸化物であるアルカリ蓄電池である。本発明の第7は、前記第4の発明の希土類元素の単体または化合物が、前記セパレータの少なくとも正極に接する側の面に塗布されているアルカリ蓄電池である。本発明の第8は、前記第1又は第4の発明の希土類元素の単体または化合物の塗布量が、正極活物質量に対して0.1重量%～10重量%であるアルカリ蓄電池である。

【0006】イッテルビウムまたはイッテルビウム化合物はアルカリ水溶液中でわずかに溶解し、安定な水酸化物として析出する。イッテルビウム水酸化物は高温時の酸素過電圧を引き上げる効果を持ち、充電末期における

正極側からの酸素ガス発生を抑制するため、高温での利用率を高めることができる。また、イッテルビウム等の希土類元素の単体または化合物を添加すると、電解液中にわずかに溶出した希土類元素イオンが水素吸蔵合金電極表面に安定な水酸化物として析出する際に被膜を形成し、これが合金の腐食を防ぐため電池寿命が伸びる。これらの作用は希土類元素一般に見られるが、特にイッテルビウムはその効果が大きい。

【0007】一方、イッテルビウムまたはイッテルビウム化合物の溶解抑制効果はコバルト化合物にも及び、コバルト化合物が溶解してなる HCO_2^- イオンの生成の抑制まで行ってしまう。そうなると1サイクル目の充電により形成される CoOOH による活物質間の導電性ネットワークの形成が不十分となってしまい、利用率低下や高率放電性能低下を引き起こす。しかし、イッテルビウムまたはイッテルビウム化合物の正極表面への塗布は、イッテルビウムまたはイッテルビウム化合物とコバルト化合物との距離を離すことで、極板内部のコバルト化合物の溶解を抑制することなく、導電性ネットワーク形成を確実に行うことができるため、上記のような弊害はなくなる。

【0008】また、イッテルビウムまたはイッテルビウム化合物の塗布量は正極活物質質量に対して0.1重量%～10重量%が望ましい。0.1重量%以下であると酸素過電圧上昇効果が得られず、10重量%以上であると溶解抑制効果が大きすぎて導電性ネットワークの形成不良や、負極の水素吸蔵合金の活性化が遅延するなどの弊害が現れる。

【0009】また、セパレータ表面に希土類元素の単体または化合物を塗布することによっても同様に水酸化ニッケルの酸素過電圧を適切に高くすることができる。その上、コバルト化合物の溶解析出により形成される導電性ネットワークに悪影響を及ぼすことがないため、ニッケル電極の利用率低下や高率放電性能低下を引き起こすこともない。また、ニッケル電極中の真の水酸化ニッケル充填量を削減することもないため、電極容量ないしは電池容量が低下してエネルギー密度が低下してしまうこともない。

【0010】従って、これらの方法を用いてアルカリ蓄電池を作製することにより、ニッケル電極の放電電位や電極容量、エネルギー密度を低下させることなく高温下での充電効率の低下を抑制し、広範囲の温度下における充放電効率に優れたアルカリ蓄電池を提供することができる。

【0011】

【発明の実施の形態】以下、実施例に基づき本発明を説明する。

【0012】(実施例1) 正極活物質として Zn , Co を固溶体添加した高密度水酸化ニッケルを準備し、導電補助剤として一酸化コバルト(CoO) 10重量%を充

分混合し、これに増粘剤を加えペースト状にし、3次元多孔体ニッケル基板に充填、乾燥後所定の厚みにプレスして正極板を得た。これに酸化イッテルビウム(Yb_2O_3)と増粘剤を混合したペーストを水酸化ニッケル量に対して2.5重量%となるように塗布し、再度乾燥して本発明電極とした。また、上記と同様の手順で酸化イッテルビウムを塗布しない通常の電極を作製し、比較電極Ⅰとした。さらに、 Zn , Co を固溶体添加した高密度水酸化ニッケルに一酸化コバルト10重量%、酸化イッテルビウム2.5重量%を充分混合し、これに増粘剤を加えてペースト状にし、3次元多孔体ニッケル基板に充填、乾燥後所定の厚みにプレスして正極板を得た。これを比較電極2とした。

【0013】このようにして作製した本発明電極、比較電極Ⅰおよび比較電極2を水素吸蔵合金電極を対極として、電解液として比重1.28の水酸化カリウム水溶液、参照極として酸化水銀電極を用いて電解液過剰下で充放電試験(充電0.1C、放電0.2C)を行った。図1に充放電結果を示す。本発明電極は酸化イッテルビウムを塗布しない比較電極Ⅰに比べて利用率が高く、特に50℃および40℃の高温においてはその差が顕著に現れた。また、酸化イッテルビウムを混合した比較電極2でも本発明電極と同等の利用率を示した。

【0014】図2に本発明電極と比較電極Ⅰの20℃および50℃の充電曲線を示す。20℃においては酸素過電圧は同程度であるが、50℃においては比較電極Ⅰは充電末期においても酸素過電圧の立ち上がりはなく、充電受け入れが低下していることが窺われる。一方、本発明電極においては充電末期において酸素過電圧の立ち上がりがみられ、50℃においても充電受け入れが低下していないことが窺われる。高温時の利用率維持については酸化イッテルビウムを混合した比較電極2についても同様であった。これは、塗布または混合している酸化イッテルビウムの酸素過電圧上昇効果によるものである。

【0015】図3に本発明電極、比較電極Ⅰおよび比較電極2の1サイクル目の充電曲線を示す。50～100mVに見られる平衡電位の部分は(1)式によって表される導電性ネットワーク形成反応を示している。



【0016】酸化イッテルビウムを混合した比較電極2は、平衡電位の部分が短いことから、(1)式で表される反応が短く、導電性ネットワーク形成が不十分であることが予想される。これは酸化イッテルビウムの溶解抑制効果によるものである。本発明電極ではイッテルビウムを電極表面に塗布したので、電極内部では一酸化コバルト CoO の溶解がスムーズに起こるため、導電性ネットワーク形成は十分であり、酸化イッテルビウムを含まない比較電極Ⅰと導電性ネットワークの形成はほぼ同等であった。

【0017】図4に本発明電極、比較電極Ⅰおよび比較

電極2の高率放電特性を示す。酸化イッテルビウムを混合した比較電極2は本発明電極および比較電極1に比べ高率放電特性の低下が大きい。上述のように導電性ネットワークの形成が不十分なため高率放電特性が大きく低下したためと考えられる。本発明電極は導電性ネットワークの形成が十分であるので、高率放電性能の大きな低下は見られなかった。

【0018】(実施例2)まず、市販のポリオレフィン系不織布の両面に、酸化イッテルビウム(Yb_2O_3)と増粘剤を溶解した水溶液を混合してペースト状にしたものを均一に塗布し、乾燥させたものを作製した。これをセパレータとし、Zn、Coを固溶体添加した高密度水酸化ニッケル粉末に導電補助剤として一酸化コバルト(CoO)10重量%を混合したものを3次元多孔体ニッケル基板に充填し、乾燥後所定の厚みにプレスして作製したニッケル電極を正極とし、水素吸蔵合金を3次元多孔体ニッケル基板に充填し、乾燥後所定の厚みにプレスして作製した水素吸蔵合金電極を負極として正極容量規制の電極群を構成し、電解液として比重1.28の水酸化カリウム水溶液を用いて、密閉形ニッケル-水素化物蓄電池を作製し、本発明電池Aとした。

【0019】(実施例3)さらに、上記実施例2と同じ市販のポリオレフィン系不織布の片面に、酸化イッテルビウムと増粘剤を溶解した水溶液を混合してペースト状にしたものを均一に塗布し、乾燥させたものを作製した。これを酸化イッテルビウムを塗布した面をニッケル電極と接するように用いてセパレータとし、その他の条件は実施例2と同一とした本発明電池Bを作製した。

【0020】(比較例)また、上記実施例3と同じく片面に酸化イッテルビウムを塗布したものを用いて、酸化イッテルビウムを塗布した面を水素吸蔵合金電極と接するように用いてセパレータとし、その他の条件は実施例2と同一とした比較電池Cを作製した。

【0021】(従来例)一方、上記実施例及び比較例と同じ市販のポリオレフィン系不織布をそのままセパレータとし、その他の条件は実施例2と同一とした従来電池Dを作製した。

【0022】このようにして作製した各種電池は、常温で注液後4.8時間放置した後、ニッケル電極の理論容量の0.1C相当の電流で1.5時間充電、0.2C相当の電流で両極間電位が1Vに至るまで放電を1サイクルとするものを5サイクル繰り返し、充分に活性化を行った。その後これらの電池を用いて充放電試験を行った。

【0023】まず、上記した本発明電池A、B、比較電池C、従来電池Dについて、温度特性試験を行った結果を図5に示す。なお、試験条件は、各種温度下で、ニッケル電極の理論容量の0.1C相当の電流で1.5時間充電した後、0.2C相当の電流で両極間電位が1Vに至るまで放電したものである。図5より、本発明電池A、B、比較電池Cでは高温充放電時にも充分な容量を保持

しており、かつ、常温に戻したときの容量回復も良好であることが分かる。また、この効果は酸化イッテルビウムを塗布した面をニッケル正極に接するように用いた本発明電池A、Bにおいて特に顕著であることも分かる。これは、酸化イッテルビウムをセパレータに塗布したことにより、水酸化ニッケルの酸素過電圧が高くなるため、充電反応と酸素ガス発生反応の電位差を大きくすることができ、充電効率を向上させることができたためであると考えられる。

【0024】更に、上記した本発明電池A、B、比較電池C、従来電池Dを試験終了後に解体し、ニッケル正極および水素吸蔵合金負極から放電末の活物質をそれぞれ取り出し、水洗乾燥した後、X線回折により分析を行った。

【0025】まず、ニッケル正極活物質のX線回折パターンおよびその一部を拡大したものを図6に示す。なお、参考として、図6にはニッケル正極活物質原料を混合した状態でのX線回折パターンの一部を拡大したものも示す。図6から明らかのように、本発明電池A、B、比較電池C、従来電池Dいずれも $\beta-Ni(OH)_2$ のピークが主であり、導電補助剤として混合した一酸化コバルト(CoO)のピークはほとんど見られない。これは、本発明電池A、B、比較電池Cのいずれにおいても、酸化イッテルビウムの溶解抑制効果による一酸化コバルトの溶解析出の妨害がそれほど大きく影響することなく、コバルト導電性ネットワークの形成が十分に行われていることを示す結果である。

【0026】次に、水素吸蔵合金負極活物質のX線回折パターンの内、一部を拡大したものを図7に示す。なお、参考として、図7には充放電前の水素吸蔵合金のX線回折パターンの一部も示す。図7から明らかのように、従来電池Dでは $2\theta = 27^\circ \sim 29^\circ$ 付近に合金の腐食による希土類水酸化物のピークが現れているが、本発明電池A、B、比較電池Cのいずれにおいてもこのピークが小さく、合金の腐食が抑制されていることが分かる。

【0027】以上より、本発明電池A、Bは、比較電池Cおよび従来電池Dに比較して、ニッケル電極の放電電位や電極容量、エネルギー密度を低下させることなく高温下での充電効率の低下を抑制し、広範囲の温度下における充放電効率に優れただけでなく、水素吸蔵合金負極の合金腐食を抑制し、サイクル寿命に優れたニッケル-水素化物蓄電池であることがわかる。

【0028】なお、本実施例では、酸化イッテルビウム(Yb_2O_3)を用いたが、水酸化イッテルビウム($Yb(OH)_3$)を用いた場合や、酸化エルビウム(Er_2O_3)、水酸化エルビウム($Er(OH)_3$)を用いた場合にも同等の効果が得られる。また、他の希土類元素についても効果が得られる。本実施例ではニッケル-水素化物蓄電池を作製したが、ニッケル-カドミウム蓄

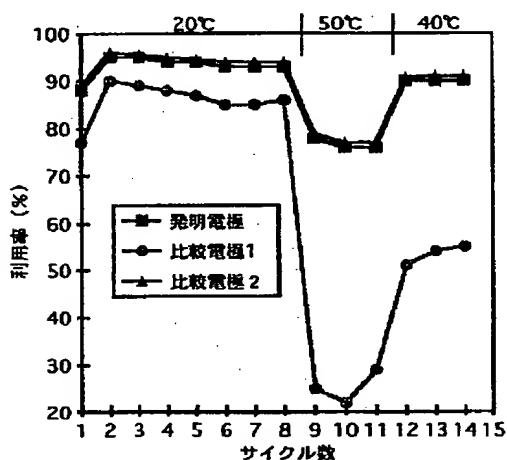
電池や、ニッケル-亜鉛蓄電池などの水酸化ニッケルを主成分とするペースト式ニッケル電極を正極として用いたアルカリ蓄電池であれば同等の効果が得られる。

【0029】

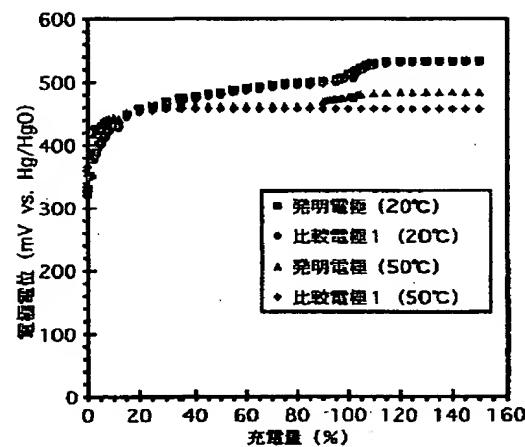
【発明の効果】上記のように、本発明のアルカリ蓄電池により、広範囲の温度下におけるニッケル正極の利用率を高め、高温下での利用率の低下を抑制し、初充電における導電性ネットワークの形成も十分であるので高率放電特性を高め、安定した容量特性および優れたサイクル性能が得られるという極めて優れた効果が得られる。

【図面の簡単な説明】

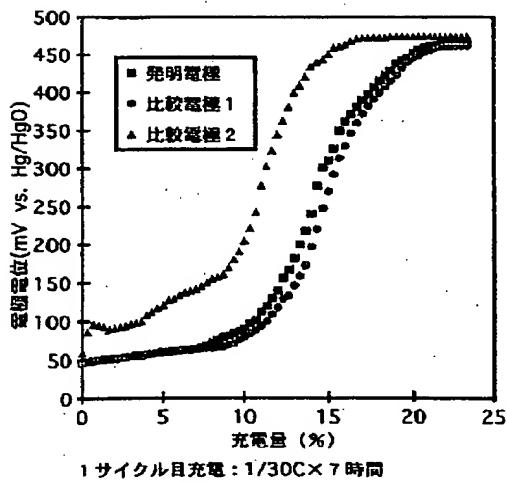
【図1】



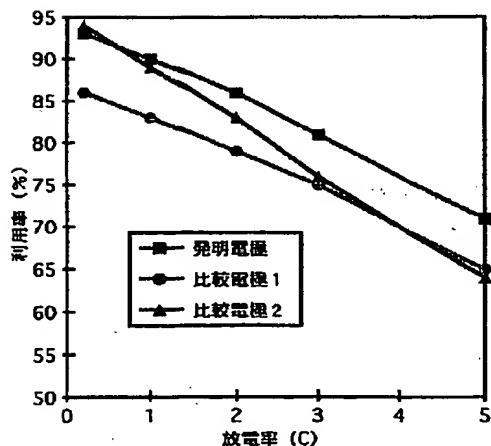
【図2】



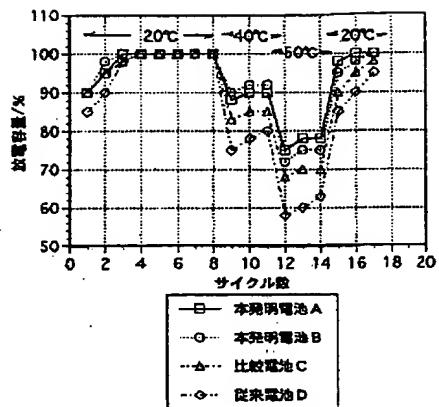
【図3】



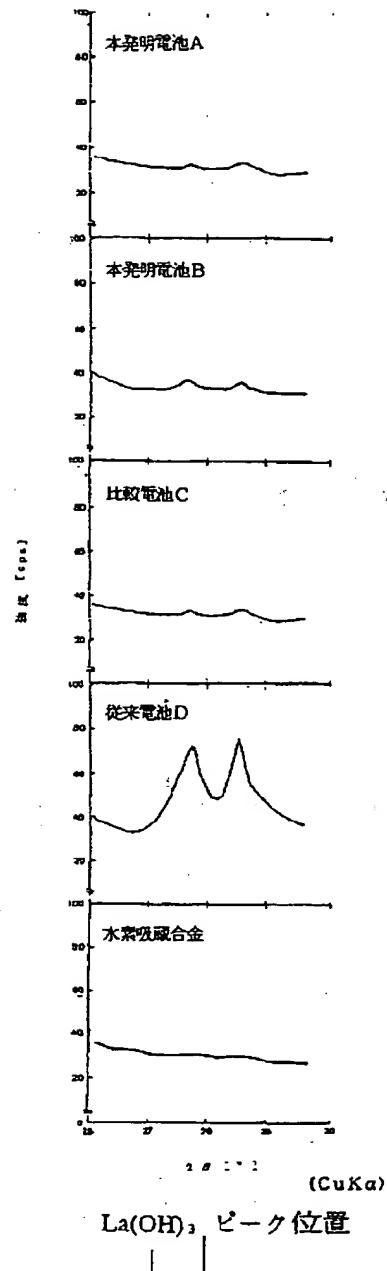
【図4】



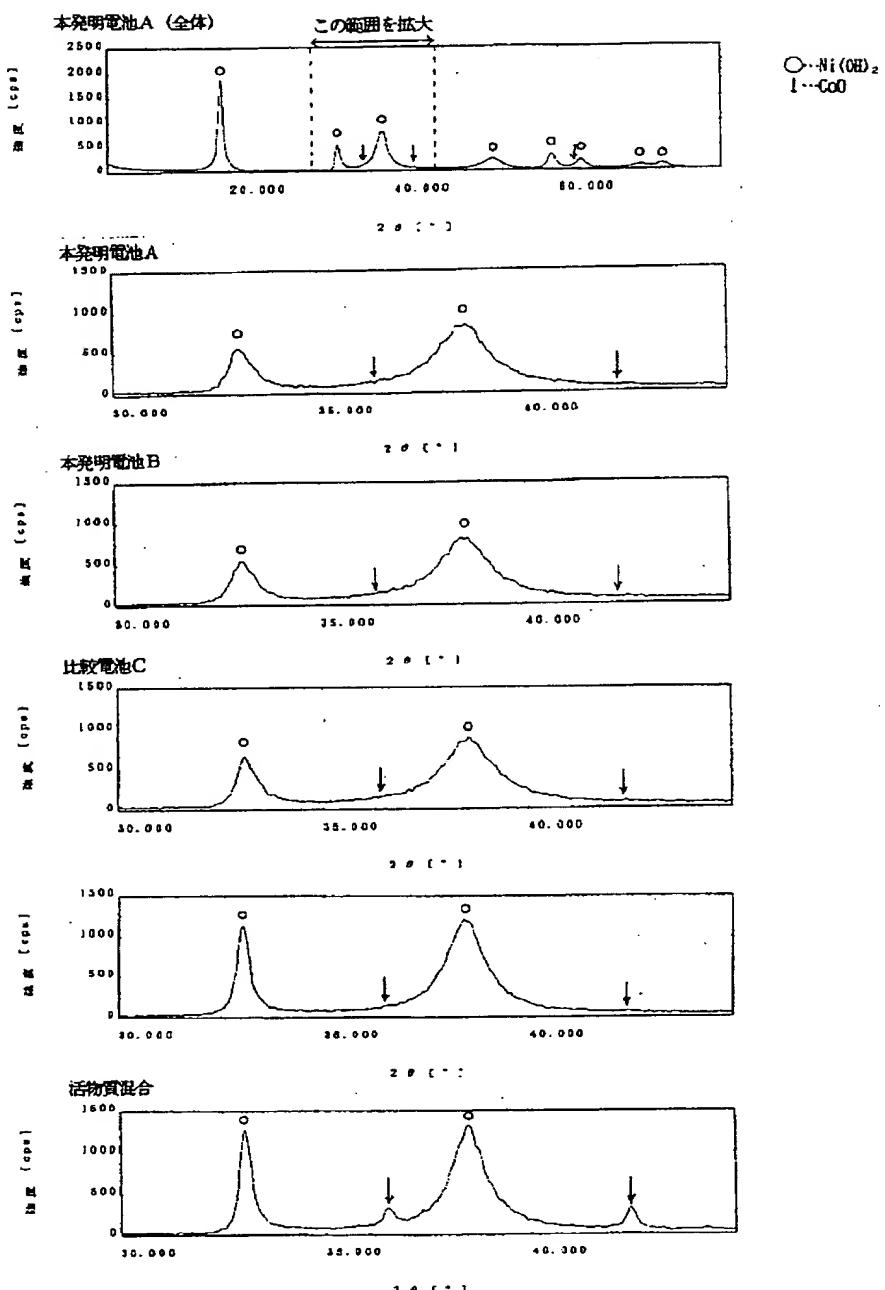
【図5】



【図7】



【図6】



フロントページの続き

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